Counterion-Induced Attraction between Rigid Polyelectrolytes

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We report on results of long-time Brownian-dynamics simulations of electrostatic interactions between two rigid polyelectrolyte rods. We find that the interaction can be both repulsive, as obtained from mean-field theory, and attractive. The onset of attraction depends not only on the fixed charge density of the rod, but also on its radius. The attractive force is found to be due to the development of positional correlations between the counterions condensed on the two rods, for which we propose a simple analytical model. [S0031-9007(97)02764-6]

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Electrostatic forces constitute an important contribution to the interaction between colloidal particles and macromolecules in aqueous media [1]. Two macromolecules with like charge would naturally be expected to repel each other. Indeed, cylindrical macro-ions ("polyelectrolytes"), such as DNA strands in water containing (monovalent) salt [2,3], repel each other. Furthermore, according to the widely used mean-field theory of electrostatic interactions between macro-ions—the Poisson-Boltzmann (PB) theory [1]—two parallel cylinders with the same line charge always should repel each other [4]. However, a series of experiments on charged biopolymers, including DNA [2,3], F-actin fibers [5], microtubules [5], and aggregating viruses [5], indicate that in the presence of small amounts of *polyvalent* salts, the electrostatic interaction is either attractive—in violation of basic PB theory—or so weakly repulsive that attractive forces of a different origin (e.g., hydrophobic or hydration interactions) overwhelm electrostatic repulsion. These experiments are usually analyzed in terms of a dimensionless quantity ξ (the "Manning parameter"), defined by the ratio of the two fundamental lengths in the problem: $\xi = l_B/b$. Here, $l_B = e^2/\varepsilon k_B T$ is the Bjerrum length (of order 7.1 Å at room temperature for $\varepsilon \approx 80$ the dielectric constant of water) and $1/b$ is the line density of fixed charges along the polyelectrolyte. The Manning parameter can also be interpreted as the ratio of the characteristic monovalent electrostatic energy to the thermal energy $k_B T$. According to the Manning criterion [6], because of condensation of the small mobile ions ("counterions") onto the polyelectrolyte, the *effective* charge per unit length is only a fraction $1/Z\xi$ of its "bare" value (Z is the counterion valency). An experimental rule of thumb for the disappearance of electrostatic repulsion between DNA strands is that the effective charge per unit length should be less than 10% of its bare value.

It has been known for over a decade now, from both simulation and integral equation approaches, that short-range correlations between the counterions (not included in PB theory) can lead to attractive corrections to the PB result [7]. Nevertheless, there is still no closed-form expression available for the electrostatic interaction between two charged rods which includes counterion correlations, nor is there even any general consensus about this physical origin of this attraction. Oosawa [8] has given a simple argument suggesting that *in the limit of very large distances R* between two parallel charged rods, the force per unit length $f(R)$ should be

$$f(R) \cong k_B T\left(\frac{1}{Z^2 l_B R} - \frac{(Z\xi)^2}{1 + (Z\xi)^2}\frac{1}{R^2} + \dots\right). \quad (1)$$

The first term in Eq. (1) is the ξ-independent PB repulsion while the second term describes—to lowest order [see discussion following Eq. (4) below]—the effects of long-wavelength correlated charge-density fluctuations on the two rods. Note that crossover from repulsion to attraction as a function of R takes place when R becomes less than the Bjerrum length.

To examine the nature of the electrostatic interaction between stiff polyelectrolytes, we have performed Brownian dynamics (BD) simulations of a minimal particle model: two parallel, uniformly charged rods with compensating counterions and no added salt [9]. Along the rods, we used periodic boundary conditions with a repeat length L_z. To vary the parameter $Z\xi = |q_{\rm rod}|q_{\rm ion}/\varepsilon b k_B T$, we kept the counterion charge $q_{\rm ion}$ fixed at $+2e$ while the charge per unit length $q_{\rm rod}/b$ of the rods was varied (with b fixed at 1.7 Å). Overall charge neutrality was maintained by requiring that the repeat length is related to the number of counterions through $2|q_{\rm rod}|L_z/b = q_{\rm ion}N$ (the factor of 2 is due to the fact that we have two rods). We checked for finite size effects by repeating the simulations for $N = 80$ and $N = 160$ with no detectable difference between the results of the two simulations. The number of counterions was limited by the computation time, due to the long-range nature of the Coulomb interaction requiring full evaluation of the sum of all pair contributions at every computational time step. More explicitly, each counterion interacts Coulombically not only with a second particle but also with its counterparts in *all* periodic boundary conditions cells [10]. To reach a sufficient level of thermal equilibration, a large number of time steps was required (up to 10^9 for large R). Apart from the Coulomb interaction, we also included a $1/r^{12}$ repulsive interaction between the counterions and the rod charges. The resulting ion-rod potential has a minimum at a distance r_0 from the rod center. We may consider $(q_{\rm rod} q_{\rm ion}/\varepsilon r_0)$ as a measure of the specific ionic binding energy between a counterion and a rod ion. We thus have two characteristic length scales in the simulation: $b(= l_B/\xi)$ and r_0. Note that only b appears in the Oosawa theory, whereas we shall argue that it is crucial to feature r_0 as well.

In Fig. 1 we show the results of a BD simulation near $T = 300$ K with $r_0 = 4.2$ Å (corresponding to a typical ionic bonding energy of order a few $k_B T$). The mean force $\langle F_{12} \rangle$ per repeat length b is plotted versus R for three different values of $q_{\rm rod}$. $\langle F_{12} \rangle$ is the total force on each rod, due to the other rod and to all mobile charges, averaged over counterion configurations corresponding to a given separation distance R, rod charge density $q_{\rm rod}/b$, and temperature T. As our condition for thermal equilibration, we demanded that $\langle F_{12} \rangle_{\text{left-rod}}$ should be constant and equal to $\langle F_{12} \rangle_{\text{right-rod}}$ within a preset numerical accuracy.

We see from Fig. 1 that large attractive forces of appreciable range indeed appear as we increase $q_{\rm rod}$ (and hence $Z\xi$). This demonstrates that even in our simple "minimal" model, attractive electrostatic forces appear as the counterion valency is increased. The range of values of $|q_{\rm rod}|$ over which we encounter attractions is shown in Fig. 2. In contrast to what is expected from either the Oosawa theory or the rule of thumb, the onset of attraction is *highly sensitive* to r_0, the equilibrium spacing between a counterion and a rod. The Manning parameter clearly is not the sole control parameter determining the onset of electrostatic attraction. We then studied the dependence of the maximum value of the attractive force, $|\langle F_{\rm min} \rangle|$ (see Fig. 1), on temperature T. According to Eq. (1), we should expect $|\langle F_{\rm min} \rangle|$ to increase linearly with temperature. As shown in Fig. 3, $|\langle F_{\rm min} \rangle|$ is seen to strongly *decrease* with increasing temperature, indicating that the attractive forces encountered in our simulations are not accounted for by the standard Oosawa theory.

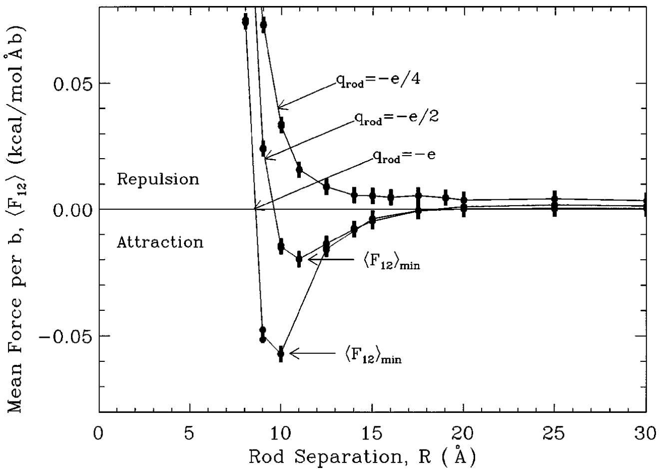

FIG. 1. Mean force $\langle F_{12} \rangle$ (per length b) between two parallel charged rods, with divalent counterions, as a function of the rod separation distance R for temperature $T \approx 300$ K, ionic radius $r_0 \approx 4.2$ Å, system size L_z, and different values of the rod charge $q_{\rm rod}$ (per 1.7 Å). The effective Manning parameter $Z\xi = |q_{\rm rod}| q_{\rm ion}/\varepsilon b k_B T$ and system size are respectively: $Z\xi = 2.1$ and $L_z = 544$ Å, with $q_{\rm rod} = -e$. The estimated statistical uncertainty is always less than indicated by the error bars.

The actual origin of the attraction is evident from an examination of the structure of the condensed counterions at lower temperatures: they from two interlocking structures, resembling Wigner crystals [11], arranged around the two cylinders (see inset Fig. 3). The precise structure of the Wigner crystals is sensitively dependent on R, r_0, and other parameters. In the low temperature limit, we *always* encounter electrostatic attraction, independent of the valency of the counterions. This simply reflects a general feature of the electrostatics of charged particles. Whether this attraction survives up to room temperature *does* depend on the counterion valency (and other physical parameters). With increasing temperature, the two Wigner crystals lose long-range positional order, but *short*-range order survives up to surprisingly high temperatures. *It is this residual positional order on the two rods, which is correlated for small R, which gives rise to the attractive force at finite temperatures.*

To analytically describe attraction by short-range structural order [12], we considered the $r_0 = 0$ limit where all the counterions are condensed on two parallel lines. In that case, our model reduces to two (one-dimensional)

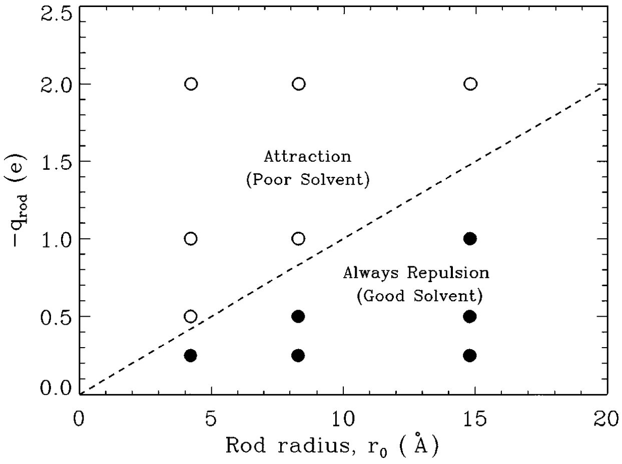

FIG. 2. Regimes of rod charge $q_{\rm rod}$ (per 1.7 Å) and ionic radius r_0 where attraction (open circles) and repulsion (closed circles) are found, again for divalent counterions.

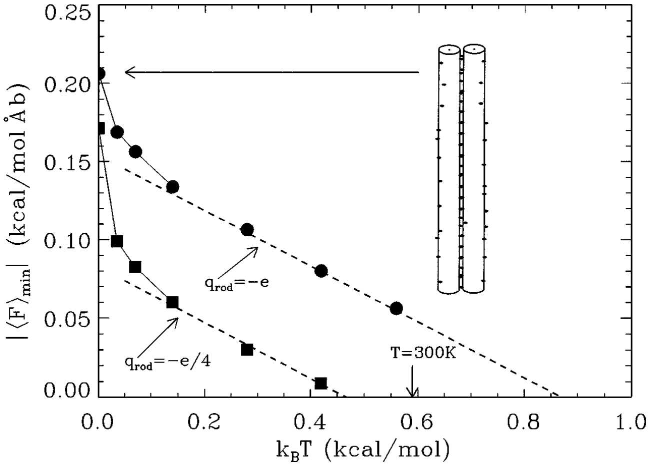

FIG. 3. Dependence of the maximum attractive force $|\langle F_{\min}\rangle|$ (per rod charge q_{rod}) between the rods, as a function of temperature T, for $q_{\mathrm{rod}} = -e$ (top curve) and $q_{\mathrm{rod}} = -e/4$ (bottom curve). The error in the data is comparable to the size of the circles and squares indicating the results. Inset: Counterion arrangement in the low-temperature limit for $q_{\mathrm{rod}} = -e$. (Some counterions are obscured by the rods and are not shown here.)

one-component plasmas (OCP's), interacting electrostatically. The effective Hamiltonian for Gaussian number density fluctuations of the two coupled OCP's is

$$H = \frac{1}{2L}\sum_k [|n_1(k)|^2 + |n_2(k)|^2]S(k)^{-1}k_BT + \frac{(Ze)^2}{2\varepsilon}\int dz_1 \int dz_2 \frac{n_1(z_1)n_2(z_2)}{\sqrt{(z_1 - z_2)^2 + R^2}}\,. \qquad (2)$$

Here, $n_{1,2}(z)$ and their Fourier transforms $n_{1,2}(k)$ describe counterion densities on lines 1 and 2, respectively, while $S(k)$ is the liquid structure factor of an isolated OCP [13]. If we compute the free energy perturbatively to second order in the interaction between the OCP's, we find the following rod-rod interaction free energy per unit length:

$$U(R) = -\frac{(Ze)^4}{2\pi\varepsilon^2 k_BT}\int_0^\infty dk S(k)^2 K_0^2(kR)\,, \qquad (3)$$

with K_0 the zero order modified Bessel function. In the relevant low-temperature regime, where $Z\xi = (Ze)^2/\varepsilon a k_BT$ is large compared to one, the OCP structure factor essentially consists of a sequence of Lorentzian peaks centered at $k_m = m(2\pi/a)$, with m an integer and $a = Zb$ the mean spacing between the counterions. Each peak has a width $\Delta k_m \cong (\pi^2/2)a^{-1}m^2/(Z\xi \ln Z\xi)$ proportional to k_BT. The interaction free energy in the limit of large $Z\xi$ (and fixed R) is dominated by the contribution to the integral over k in Eq. (3) coming from the first few peaks in the structure factor,

$$U(R)a/k_BT \approx -(Z\xi)^3 \ln(Z\xi) K_0^2(2\pi R/Zb)\,. \qquad (4)$$

As opposed to Eq. (1), this attractive interaction indeed increases with decreasing temperature (as T^{-2}, since $\xi \propto T^{-1}$). Moreover, as a function of R it decreases exponentially for larger R with a decay length of $Zb/4\pi$. Finally, as opposed to the attractive term in Eq. (1), $U(R)$ is also quite sensitive to the counterion valency: it is proportional Z^2 while the range increases linearly with Z.

The relation of Eq. (3) to Oosawa's result is found by keeping $Z\xi$ fixed in Eq. (3) and going to the limit $R \to \infty$. In that case, the dominant density fluctuations contributing to $U(R)$ come from the long-wave length regime rather than from the peaks in the structure factor. In that limit, Eq. (3) indeed reproduces the second term of Eq. (1). Equation (3) should thus be considered as a generalization of Oosawa's result to smaller R values. It is clear though that the attractive forces encountered in the simulations are better described by Eq. (4) than by Eq. (1). If the free energy associated with H is computed nonperturbatively, one finds that Eq. (4) only holds provided $(Z\xi)^2 K_0(2\pi R/Zb)$ is small compared to one, i.e., still at larger R values. However, our numerical precision for larger R is not sufficient for obtaining a quantitative comparison between Eq. (4) and the data. Moreover, the extension of the theoretical analysis to finite values of rod and counterion radii is rather nontrivial.

In summary, we have shown that in a minimal model of electrostatic interaction between stiff polyelectrolytes, attractive interactions appear at higher counterion valencies. The onset of the attraction depends sensitively on the small distance "cut-off" r_0, i.e., on the counterion-rod radius. We have developed a simple analytical expression to account for an attraction which grows with decreasing temperature. Finally, we note that the results for the minimal model cannot be directly applied to biopolymers since we do not include the actual molecular architecture of a biopolymer, nor interactions other than electrostatics, nor a proper model for the structure of water, etc. Because of the critical dependence of our results on r_0, we indeed expect the collapse point of actual biopolymers to be sensitive to the finite size of the counterions—as is observed experimentally [5]—to molecular architecture, as well as the short-range properties of the interatomic potentials (e.g., hydration effects). Nevertheless, our results indicate that large attractive forces generically will appear in a simple model and they may well be responsible for the collapse of stiff biopolymers in the presence of polyvalent counterions.

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